

# MERCURY INFORMATION **CLEARINGHOUSE**



**Quarter 2 - Mercury Measurement**

**April 2004**



Canadian Electricity Association  
Association canadienne de l'électricité



**EERC**

Energy & Environmental Research Center



## **MERCURY INFORMATION CLEARINGHOUSE**

### **QUARTERLY 2 – MERCURY MEASUREMENT**

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## **MERCURY INFORMATION CLEARINGHOUSE**

### **QUARTERLY 2 – MERCURY MEASUREMENT**

#### **EXECUTIVE SUMMARY**

Mercury is an immediate concern for the Canadian and U.S. electric power industries as a result of pending regulation of mercury emissions. Canada has established a consultative process to develop Canadawide Standards (CWS) for mercury emissions from coal-fired electricity generation. In the United States, the Proposed Utility Mercury Reduction Rule comment period has been extended until June 29, 2004, at which time the U.S. Environmental Protection Agency (EPA) will be reviewing input from industry and environmental groups and developing a final rule.

With mercury regulations pending and with the early stages of full-scale demonstration of control technologies, measurement of mercury in combustion flue gas is of critical importance to demonstrate compliance and to allow evaluation of mercury control technologies. However, collecting a representative flue gas sample for mercury analysis presents many challenges owing to complex flue gas chemistry, high temperatures, mercury reactivity, and particulate loading. Given these challenges, many methods and instruments are available under varying degrees of development and are addressed in this quarterly report.

The most common approach for measuring mercury emissions from anthropogenic point sources consists of sampling train methods. Several common impinger-based methods include EPA Method 29, the tris buffer method, the Research Triangle Institute (RTI) method, and the Ontario Hydro method. Each of these methods relies upon an isokinetic nozzle and filter to collect a flue gas sample which is transported through a variety of liquid and solid sorbents to separate and preconcentrate gaseous mercury species. Quantification of the collected mercury species is then conducted using cold-vapor atomic absorption spectroscopy (CVAAS), cold-vapor atomic fluorescence spectroscopy (CVAFS), or energy-dispersive x-ray fluorescence (EDXRF).

A similar sample collection approach can also be applied to capture mercury species on a solid sampling medium through adsorption, amalgamation, diffusion, or ion exchange. These methods offer advantages in easier handling and greater stability; however, they are limited to time-averaging applications.

Real-time data collection can only be obtained through mercury continuous emission monitors (Hg CEMs). A large variety of Hg CEMs are available utilizing a variety of flue gas conditioning approaches; however, all commercially available instruments measure elemental mercury and are based on one of the following methods: preconcentration by gold amalgamation with CVAAS, Zeeman-modulated CVAAS, or preconcentration by gold amalgamation with CVAFS detection. Development work is ongoing for instruments that use atomic emission spectroscopy (AES) and laser technologies. As they are currently configured, Hg CEMs possess several challenges to long-term, low-maintenance operation, the most significant of which include sample collection and flue gas conditioning. Mercury species reactivity and particulate

loading make transporting a representative gas sample to the instrument a challenge and require heated sample lines and particulate removal techniques which prevent the buildup of a filter cake. Flue gas conditioning is an area where the greatest development is needed. Wet chemistry methods have typically been used to convert mercury to the elemental form that the analyzer can detect. These solutions are corrosive or caustic chemicals and challenges associated with their use are considered the limiting factor in Hg CEM reliability. Efforts to develop dry conversion units are beginning to produce results and focus on high-temperature catalysts and thermal reduction to convert oxidized mercury to the elemental form for analysis. It is anticipated that developments in this area will be the critical factor in ensuring real-time mercury measurements can be conducted reliably under steady-state operation.

## **MERCURY INFORMATION CLEARINGHOUSE**

### **QUARTERLY 2 – MERCURY MEASUREMENT**

#### **INTRODUCTION**

The Canadian Electricity Association (CEA) identified a need and contracted the Energy & Environmental Research Center (EERC) to create and maintain an information clearinghouse on global research and development activities related to mercury emissions from coal-fired electric utilities. With the support of CEA, the Center for Air Toxic Metals® (CATM®) Affiliates, and the U.S. Department of Energy (DOE), the EERC is developing comprehensive quarterly information updates to provide a detailed assessment of developments in mercury monitoring, control, policy, and related research advances.

Recent developments in the area of mercury regulations from coal-fired power plants in Canada in the form of Canadawide Standards (CWS) and the United States in the U.S. Environmental Protection Agency's (EPA's) Proposed Utility Mercury Reduction Rule illustrate the need for effective mercury control strategies for coal-fired electric utilities as well as standard and reliable means of measuring mercury emissions. Currently, there is a variety of measurement methods and instruments that are commercially available or under development. A



- Impact of mercury control on combustion by-products/fate of captured mercury
  - Summary of mercury-related economics for commercial systems
- Mercury chemistry and transformations
  - Mercury chemistry fundamentals, modeling, prediction, and speciation
  - Mercury fate and transport – impacts on health

One objective of this quarterly report is to provide timely information on developments in the broad field of mercury. In order to address timely issues as well as provide necessary detail on selected topics, additional subject headings will be provided to summarize recent developments not related to the quarterly topic. In this manner, updated information can be provided on topics previously covered or in advance of topics not yet discussed. The primary subject area for this quarterly report is a comprehensive review of available and developing mercury measurement methods and technologies.

## **MERCURY POLICY**

The CWS Uniform Data Collection Program is ongoing and will support standard development expected by 2005. In the United States, EPA extended the comment period for the Utility Mercury Reduction Rule until June 29, 2004, to allow interested parties 90 days to review the document and submit formal comment. Upon completion of the comment period, a more detailed review of the rule will be provided to CEA.

On December 15, 2003, EPA proposed a rule to permanently cap and reduce mercury emissions from coal-fired utilities. EPA is proposing two alternatives for controlling emissions of mercury from coal-fired utilities. The first strategy is Maximum Achievable Control Technology (MACT), and the second establishes standards of performance limiting mercury emissions from new and existing utilities. The second proposal would establish a market-based cap-and-trade program. Under the MACT provisions of the Clean Air Act, sources are given 3 years to comply with emission reduction requirements. For the power generation industry, the MACT approach raises concerns about how quickly new control technologies could be put into place. Currently, no adequately demonstrated control technologies are specifically designed to reduce mercury emissions from coal-fired utilities. Also, the short compliance window would preclude the effective use of developing technologies. Under the cap-and-trade approach, EPA would allocate allowances for mercury emissions to each state which would then allocate them to utilities. The utilities would then be allowed to trade or bank any allowances above those required to cover their emissions each year. With the cap-and-trade program, emissions monitoring and reporting requirements will be stringent. However, this will allow for flexibility in trading which will create financial incentives for utilities to look for new and low-cost ways to reduce mercury emissions. Relative to the cap-and-trade system, MACT would restrict the options and incentives for power plants to achieve low-cost reductions. These higher costs could lead to increased electricity prices.

## QUARTERLY 2 FOCUS: MERCURY MEASUREMENT

With mercury regulations pending and control technologies in the full-scale demonstration stage, measurement of mercury in combustion flue gas is of critical importance. The ability to accurately and reliably measure mercury is fundamental to demonstrating compliance when regulations are promulgated and, in the mean time, to ensuring adequate quantification of mercury removal during the full-scale demonstration and commercialization of the various mercury control technologies. Collecting a representative flue gas sample for mercury analysis from coal combustion flue gas produces many challenges. The complexity of flue gas chemistry, relatively high temperatures, reactivity of mercury species, and particulate loading must be addressed to ensure that the flue gas sample that reaches the mercury-measuring device is representative of the gas stream within the duct. In addition to measuring total mercury accurately, the identification and quantification of individual physicochemical forms (i.e., species) of mercury are imperative for addressing questions concerning mercury toxicity, bioaccumulation, emission control, and atmospheric fate and transport because each has distinctive physical, chemical, and biological properties. Mercury emissions from anthropogenic sources occur in three forms: solid particulate-associated mercury Hg(p); gaseous divalent mercury, Hg<sup>2+</sup>; and gaseous elemental mercury, Hg<sup>0</sup>.

### Sampling Train Methods

The most common approach for measuring mercury emissions from anthropogenic point sources, such as coal-fired utilities, is to extract a representative sample of the flue gas using a sampling train. Sampling trains generally consist of an isokinetic nozzle and a filter to collect a representative fly ash sample and a liquid or solid sorption system to collect a particulate-free gaseous sample. A variety of liquid and solid sorbents can be used to separate and preconcentrate gaseous mercury species. Four primary impinger-based methods have been proposed over the past 15 years to speciate mercury: EPA Method 29, the tris buffer method, the RTI (Research Triangle Institute) method, and the Ontario Hydro method. Each of these methods uses solutions intended to selectively capture the oxidized and elemental forms of mercury. EPA Method 101A is also used but was designed specifically for determining only the total emission of mercury and does not offer speciation. Cold-vapor atomic absorption spectroscopy (CVAAS), cold-vapor atomic fluorescence spectroscopy (CVAFS), or energy-dispersive x-ray fluorescence (EDXRF) is used to quantify the collected mercury species. These analytical techniques are much more standardized than the equipment and procedures to collect the mercury from the flue gas stream. Uncertainties in the selectivity and collection efficiencies of the sampling media contribute to the inaccuracy of species determinations. The sampling methods generally require extensive analyte recovery and preparation steps that may introduce contamination or result in the loss of mercury. All impinger-based methods proposed for determining mercury speciation are configured based on an EPA Method 5 or 17 template.

### *EPA Method 29*

EPA Method 29, also known as the multiple metals stack emission measurement method, was developed for measuring the solid particulate and gaseous emissions of mercury and 16 other trace elements (antimony, arsenic, barium, beryllium, cadmium, chromium, cobalt, copper, lead, manganese, nickel, phosphorus, selenium, silver, thallium, and zinc). A schematic of the

EPA Method 29 sampling train is presented in Figure 1. The EPA Method 29 sampling train consists of seven impingers. Following an optional moisture knockout impinger, gaseous mercury species are collected in two pairs of impingers connected in series containing different absorption solutions. A portion of the gaseous mercury is captured in the first pair of impingers containing aqueous solutions of 5% nitric acid ( $\text{HNO}_3$ ) and 10% hydrogen peroxide ( $\text{H}_2\text{O}_2$ ), while the remainder is captured in a second pair of impingers containing aqueous solutions of 4% potassium permanganate ( $\text{KMnO}_4$ ) and 10% sulfuric acid ( $\text{H}_2\text{SO}_4$ ). An empty impinger is located between the two sets of impingers to reduce the potential for blowback of  $\text{KMnO}_4$  into the second  $\text{HNO}_3$ – $\text{H}_2\text{O}_2$  impinger during leak checks. The last impinger in both sampling trains contains silica gel to prevent contamination and entrap moisture that may otherwise travel downstream and damage the dry-gas meter and pump.

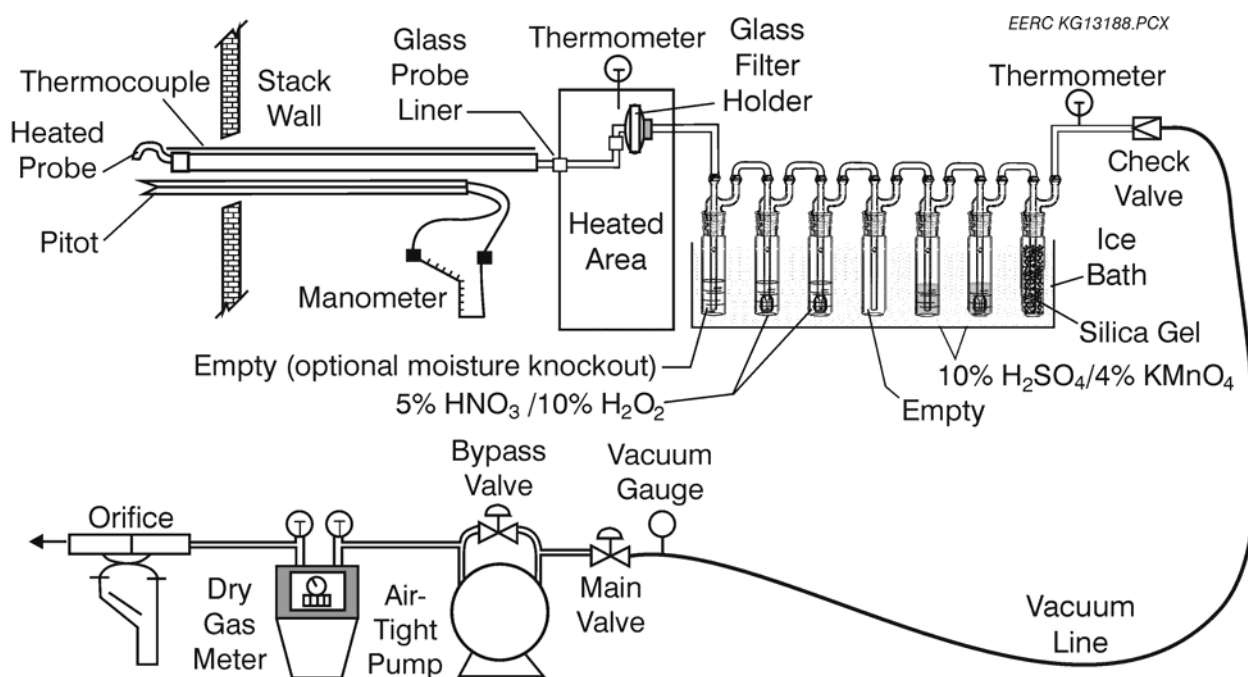


Figure 1. A schematic of the EPA Method 29 sampling train.

Although the EPA Method 29 sampling train was not originally designed for mercury speciation analysis, various research groups looked at the possibility of using the method for mercury speciation. Researchers surmised from the physical and chemical properties of mercury species that  $\text{Hg}^{2+}$  and  $\text{Hg}^0$  would be selectively absorbed in the separate acidified hydrogen peroxide ( $\text{HNO}_3$ – $\text{H}_2\text{O}_2$ ) and acidified permanganate ( $\text{H}_2\text{SO}_4$ – $\text{KMnO}_4$ ) solutions, respectively, used in the EPA Method 29 impinger train. However, investigation proved these assumptions are incorrect. Data from the validation tests indicated that the two different impinger solutions employed were not effective for reliably separating the  $\text{Hg}^{2+}$  and  $\text{Hg}^0$  forms in a chemically complex flue gas (1). As a consequence, several groups proposed modifications to the impinger solutions used in EPA Method 29. Modifications of EPA Method 29 that were tested at the EERC included the Ontario Hydro, tris buffer, and RTI methods.

### ***Tris Buffer Method***

The tris buffer method was developed by Radian International (now URS) with the support of EPRI's Environmental Control Technology Center (ECTC). A tris(hydroxymethyl) aminomethane buffer solution (abbreviated tris) is substituted for the  $\text{HNO}_3\text{--H}_2\text{O}_2$  solutions in the first set of impingers of EPA Method 29 (2). It had previously been demonstrated that tris forms trigonal complexes with  $\text{Hg}^{2+}$  in alkaline and neutral media. Testing by Radian International indicated that the addition of an ethylenediaminetetraacetic acid (EDTA) chelating agent to tris was required to effectively retain mercury chloride ( $\text{HgCl}_2$ ) (1). This method was validated using EPA Method 301 (1). A negative aspect of this modification, however, is the solution must be at a pH of 6 or higher to be effective; therefore, depending on the  $\text{SO}_2$  concentration in the flue gas, the sampling time often must be reduced to less than an hour. If the mercury or mercury species concentration is low, this may result in nondetects. In addition, recovery of mercury from the tris solution is difficult and complex. During addition of  $\text{HNO}_3$  and  $\text{H}_2\text{O}_2$  to preserve the mercury in solution, carbon dioxide is evolved rapidly, so great care must be exercised to prevent loss of the mercury-containing tris solution.

### ***RTI Method***

The RTI method modified EPA Method 29 by replacing the first  $\text{HNO}_3\text{--H}_2\text{O}_2$  impinger solution with deionized (DI) water. This method was never validated and is not used for mercury measurement.

### ***Ontario Hydro Method***

The Ontario Hydro method was developed by Dr. Keith Curtis and other researchers at Ontario Hydro Technologies, Toronto, Ontario, Canada, in late 1994. Since testing with EPA Method 29 appeared to show that some of the  $\text{Hg}^0$  was captured in the  $\text{HNO}_3\text{--H}_2\text{O}_2$  impingers, an attempt was made to more selectively capture the  $\text{Hg}^{2+}$  by substituting three aqueous 1 N potassium chloride (KCl) impinger solutions for one of the  $\text{HNO}_3\text{--H}_2\text{O}_2$  solutions. A schematic of the impinger train is shown in Figure 2. In the first tests using this concept, no acidified peroxide impingers were in the sampling train. However, it was discovered that when the sulfur dioxide ( $\text{SO}_2$ ) concentration in the flue gas was greater than approximately 750 ppm, the allowable sampling time was very short because the  $\text{SO}_2$  reacted with the  $\text{KMnO}_4$  and neutralized it. To avoid this problem, an impinger of acidified peroxide solution was used directly following the two KCl impingers. The purpose of the  $\text{H}_2\text{O}_2$  was to absorb the  $\text{SO}_2$ , thus protecting the acidified permanganate solutions. It is assumed that any mercury collected in the acidified peroxide solution was  $\text{Hg}^0$ , since the KCl solutions would collect all of the  $\text{Hg}^{2+}$ . Early testing also showed a substantial portion of the mercury was lost from the solutions (3). This was later verified in the EERC pilot-scale testing. To counter this, acidified permanganate, dichromate, or acidified peroxide solution is added to the KCl solution immediately following sampling.

Formal evaluation of the Ontario Hydro method was completed with dynamic spiking of  $\text{Hg}^0$  and  $\text{HgCl}_2$  into a flue gas stream, and the method was validated at the EERC according to EPA Method 301 (3). The Ontario Hydro method is now ASTM Method D6784-02. It has also undergone field validation at a midwestern plant burning a high-sulfur eastern bituminous coal

(4). Based on the results from the validation testing, the relative standard deviation for gaseous elemental mercury and oxidized mercury was found to be less than 11% for mercury concentrations greater than  $3 \mu\text{g}/\text{Nm}^3$  and less than 34% for mercury concentrations less than  $3 \mu\text{g}/\text{Nm}^3$ . In all cases, the laboratory bias for these tests based on a calculated correction factor was not statistically significant. These values were within the acceptable range, based on the criteria established in EPA Method 301 (% relative standard deviation [RSD] less than 50%).

In the test completed for the field validation, the quadtrain sampling resulted in a maximum variability (%RSD) of 22%. The sample recovery and analysis were done on-site, but the variability was higher than expected. However, the process variability was also high based on the plant  $\text{SO}_2$  data and mercury CEM data. Regardless, the OH method passed the statistical criteria established in EPA Method 301 (5).

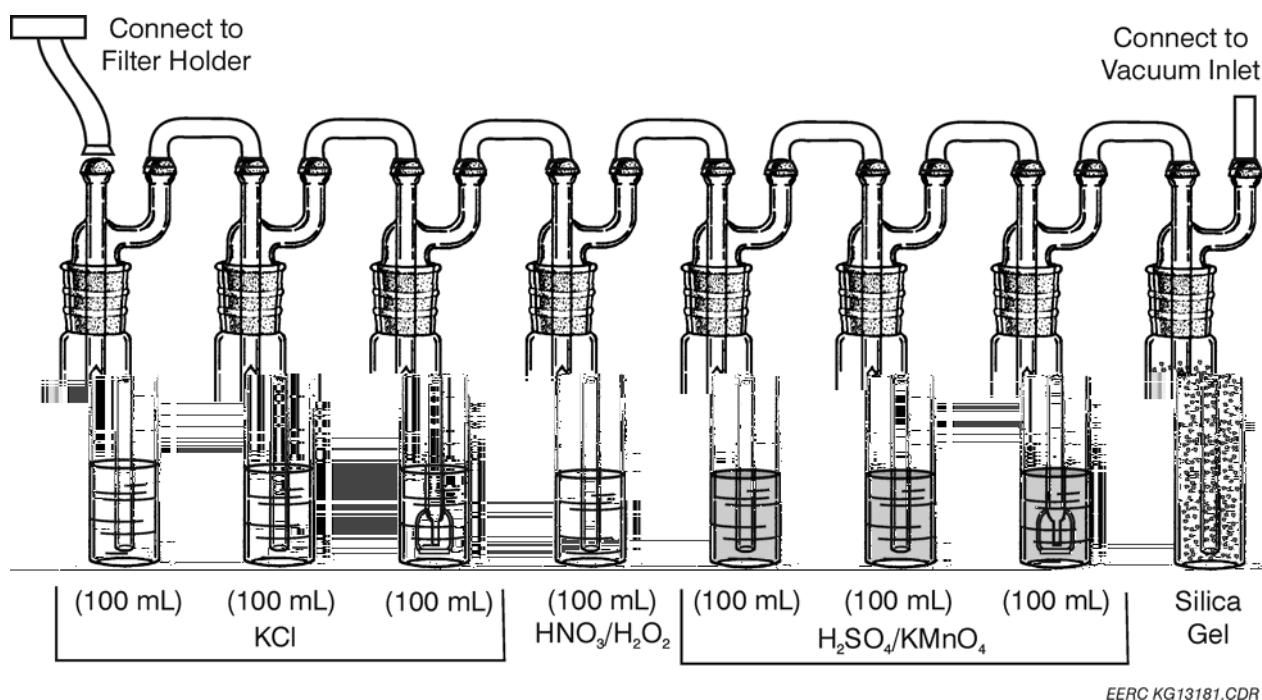


Figure 2. A schematic of the American Society for Testing and Materials (ASTM) Method D6784-02 (Ontario Hydro) sampling train.

### ***Factors to Consider in Sampling Train Methods***

The precision of particle-bound, oxidized, and elemental mercury-sampling method data is influenced by many factors: flue gas concentration, source, procedural, and equipment variables. Strict adherence to the method is necessary to reduce the effect of these variables. To ensure precise results are achieved, it is necessary that the system be leak free; all indicated system components accurately calibrated; proper sampling locations selected; glassware thoroughly cleaned; and prescribed sample recovery, preparation, and analysis procedures followed.

It should be noted that these methods were designed to be used after a plant's particulate control device. Therefore, when used with a filter in a high-dust situation (i.e., the inlet to the ESP or baghouse), reactive particulate matter can bias the speciation. This bias can be either shown as artificially high  $\text{Hg}^{2+}$  or high  $\text{Hg}(\text{p})$ .

Gaseous mercury species in flue gases that are capable of interacting with fly ash particles collected in the front half of the sampling train can produce a positive particle-bound mercury bias. Particle-bound mercury existing in the flue gas may vaporize after collection in the front half of the sampling train because of continued exposure to the flue gas sample stream and reduced pressures during the sampling period. Such vaporization would result in a negative particle-bound mercury bias.

Some of the practical limitations of the impinger-based methods originate from the problems and difficulties of using complex sample trains that are composed of relatively large amounts of glassware and tubing in the field. In addition, the glass impingers contain strongly oxidizing and acidic reagents requiring complex sample recovery and analytical procedures.

### **Dry Sorbent-Based Methods**

In addition to impinger-based sampling trains, gaseous mercury species,  $\text{Hg}^{2+}$  and  $\text{Hg}^0$ , can be selectively captured on solid sampling medium through adsorption, amalgamation, diffusion, and ion exchange processes. Solid sorbents offer several advantages relative to liquid sorbents, including greater stability and easier handling and the mercury collected can be analyzed directly using sensitive techniques such as atomic fluorescence. These advantages provide the impetus for the development of solid sorption methods. However, the dry sorbent-based methods only provide a time-averaged mercury concentration, and the sorbents must be sent to a lab for an analysis. Based on these limitations, the dry sorbent methods will not be adequate for use in a mercury emissions control loop.

Currently, two dry sorbent methods are available for mercury measurement: the flue gas mercury sorbent speciation (FMSS) method or the Quick SEM™ (QSEM) method. Both methods rely on capturing mercury on dry sorbents. The FMSS method will speciate, but the QSEM method only measures the total mercury concentration in a flue gas stream. The FMSS method was developed by Frontier Geosciences based on earlier research with the mercury speciation adsorption method for measuring total gaseous mercury in a flue gas stream. The FMSS method pulls a semi-isokinetic sample from a flue gas duct through a miniparticulate filter and a heated solid sorbent sample train. The filter and the sorbent train are analyzed to determine  $\text{Hg}(\text{p})$ ,  $\text{Hg}^{2+}$ , and  $\text{Hg}^0$  (Figure 3). The diameter of the inlet nozzle is sized to provide isokinetic flow based on the nominal duct velocity. The miniparticulate filter consisting of a small quartz fiber filter disk is inserted into a quartz tube on a pure nickel support screen to collect fly ash for  $\text{Hg}(\text{p})$  determination (6). The FMSS method sorbent train consists of dual dry sorbent traps for the gas-phase  $\text{Hg}$  species. The first trap contains dry KCl-coated quartz chips and is used to capture the  $\text{Hg}^{2+}$ . The second trap containing tri-iodine-impregnated activated carbon is used to capture the  $\text{Hg}^0$  in the flue gas stream. After sample collection, the entire sample train trap is sent to a laboratory for analysis. Analysis of the sorbent traps is conducted by CVAFS, following strong acid digestion,  $\text{BrCl}$  oxidation, aqueous  $\text{SnCl}_2$  reduction, and dual gold amalgamation (EPA Method 1631B, modified). The analysis of the  $\text{Hg}(\text{p})$  on the fly ash is done by thermal

desorption at 800°C, passing through a heated MnO converter, gold preconcentration, and CVAFS detection.

### ***FMSS Method***

The FMSS method was validated at the EERC according to a modified EPA Method 301 (7). The mean relative percent difference (RPD) was  $\pm 22\%$  for  $\text{Hg}^0$ ,  $\pm 8\%$  for  $\text{Hg}^{2+}$ ,  $\pm 10\%$  for total Hg, and  $\pm 6.5\%$  for  $\text{Hg}(\text{p})$ . The FMSS exhibited good agreement with Ontario Hydro methods, and accuracy was better than  $\pm 20\%$  for all species for the range of conditions in the validation study, including ruggedness tests. The mean accuracy of the duplicates and the triplicates for the FMSS method was better than 97% for  $\text{Hg}^{2+}$ , total Hg, and  $\text{Hg}^{2+}$ .

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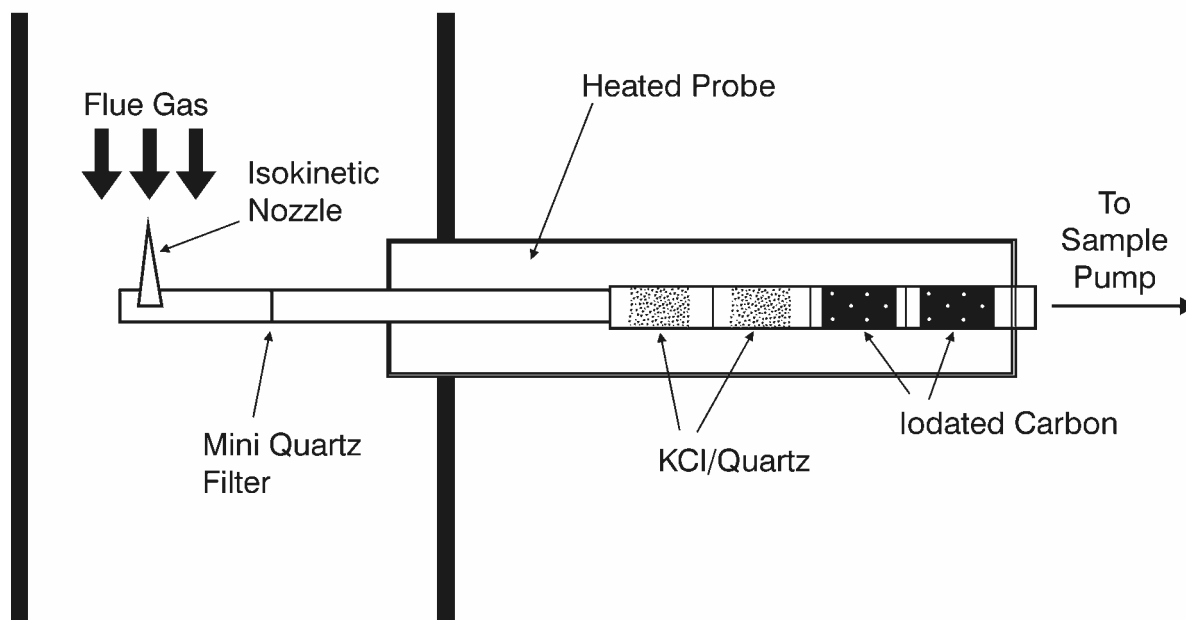


Figure 3. A schematic of the FMSS sampling train.

### ***QSEM Method***

The QSEM method was developed by EPRI, ADA Environmental Solutions, and Frontier Geosciences to measure total vapor-phase mercury mass concentration, which represents the sum of elemental and oxidized forms of mercury in a flue gas stream. A schematic of the sampling train is illustrated in Figure 4. The method is designed for use in low-dust applications with mercury concentrations ranging from 0.03 to 100  $\mu\text{g}/\text{dNm}^3$ . Known volumes of flue gas are extracted from a duct through a single or paired iodine-impregnated carbon traps. Sample recovery consists of an acid leaching of the exposed traps and the leachate analyzed by CVAFS detection. Analysis of the leachate can also be performed using CVAAS detection. Where this method is used to collect data to demonstrate compliance with a regulation, it must be performed



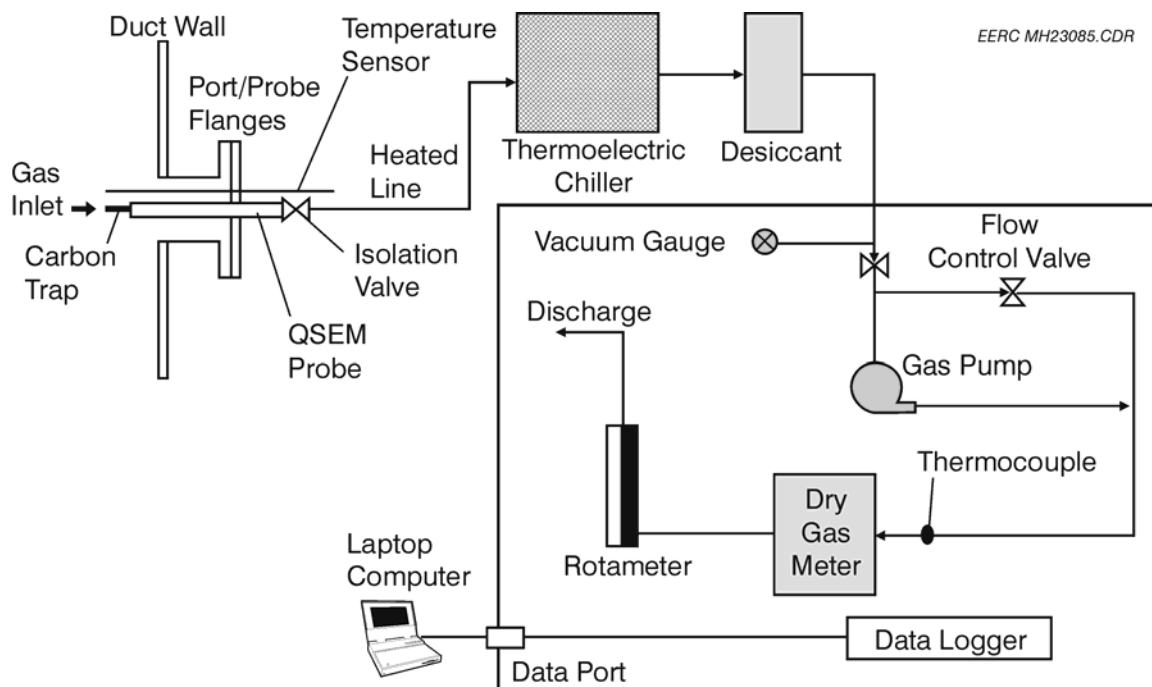


Figure 4. A schematic of the Quick SEM™ sampling train.

with paired sorbent trap equipment. The precision and accuracy of this method have not been reported, but it is inferred they are roughly the same as for the other dry sorbent method. This method is being proposed as EPA Method 324 (8).

### Mercury Continuous Emission Monitors (Hg CEMS)

The Ontario Hydro wet chemistry method and dry sorbent methods provide good results for total and speciated mercury measurements; however, these methods can fail to provide the real-time data often necessary for research and compliance. Hg CEMs are similar to other combustion system CEMs in that a sample is extracted from the gas stream, conditioned, and sent to a remote analyzer for detection. However, as stated earlier, mercury is present in three different forms ( $\text{Hg[p]}$ ,  $\text{Hg}^{2+}$ , and  $\text{Hg}^0$ ), which greatly complicates the measurement process. Although online emission analyzers can be costly to purchase, install, and maintain, they offer several benefits, including the following:

- Real- or near-real-time emission data
- Evaluation of control strategies
- Operational data for process control
- Greater understanding of process variability and operation
- Greater public assurance

As they are currently configured and utilized, Hg CEMs possess several challenges to long-term, low-maintenance continuous operation for flue gas mercury monitoring. The two main challenges include the areas of sample collection and flue gas conditioning. Collecting a representative flue gas sample for mercury analysis from coal combustion flue gas is very difficult. The complexity of flue gas chemistry, high temperatures, reactivity of mercury species, and particulate loading must be addressed to ensure that the flue gas sample that reaches the mercury-measuring device is representative of the gas stream within the duct. To a great extent, heated sample lines, gas conditioning systems, and material of construction have addressed many of these issues; however, monitoring dirty locations remains difficult, especially when reactive ash is present and traditional probe filters are used. Additionally, further development/demonstration of gas conditioning systems will be required to ensure simple, reliable, and representative flue gas monitoring can be achieved.

Hg CEMs are currently used in Europe for compliance purposes. However, a typical German power plant is equipped with two electrostatic precipitators (ESPs), two scrubbers, a spray dryer, a carbon adsorber, a catalytic oxidizer, and a baghouse to control emissions. The effects of potential interferants in the flue gas such as carbon monoxide (CO), sulfur oxides (SO<sub>x</sub>), nitrogen oxides (NO<sub>x</sub>), hydrochloric acid (HCl), ammonia (NH<sub>3</sub>), chlorine (Cl<sub>2</sub>), and particulate are almost entirely eliminated. After passing through these pollution control devices, most, if not all, of the remaining mercury is in the elemental phase (9). Measuring Hg<sup>0</sup> with all of the interfering gases removed is much easier than measuring all forms of mercury in a raw flue gas stream. Therefore, it is difficult to extrapolate European Hg CEM performance to U.S. applications. In order for Hg CEMs to be considered for regulatory compliance assurance, acceptable performance will need to be demonstrated. It is this lack of demonstrated performance that caused EPA's Office of Solid Waste to propose the use of total Hg CEMs for compliance assurance only as an option in the Phase I MACT Rule for Hazardous Waste Combustors (10). Currently the EPA has proposed a new performance standard which would outline the requirement for mercury measurement using continuous emission monitors. This Performance Specification 12A (PS-12A) titled "Specification and Test Methods for Total Vapor-Phase Mercury Continuous Emission Monitoring Systems in Stationary Sources" would be included in the U.S. Code of Federal Regulations (CFR) (40 CFR Part 60, Appendix B). However, due to the challenges identified previously with Hg CEMs, an additional sorbent based mercury measurement method, EPA Method 324, has also been proposed for inclusion in the CFR titled "Determination of Vapor Phase Gas mercury Emissions from Stationary Sources Using Dry Sorbent Trap Sampling" (40 CFR Part 63, Appendix A: Method 324). A detailed discussion of PS-12A will be provided in a future quarterly report, however a summary of criteria are included here as they are pertinent to defining the requirements of Hg CEMs.

- The Hg CEMs must be capable of measuring the total concentration in µg/m<sup>3</sup> (regardless of speciation) of vapor-phase Hg and recording that concentration on a dry basis, corrected to 20°C and 7% CO<sub>2</sub>.
- Particulate-bound Hg is not included.
- The CEMs must include a diluent (CO<sub>2</sub>) monitor and an automatic sampling system.
- Calibration techniques and auxiliary procedures are not specified.

- Procedures for measuring Hg CEM relative accuracy, measurement error, and drift are outlined.
- Hg CEM installation and measurement location specifications and data reduction procedures are included.
- Procedures for comparison with reference methods are outlined.

The basic steps that all Hg CEMs must accomplish in order to effectively measure mercury in a flue gas stream are:

- Filter particulate matter from the sample gas while minimizing flue gas fly ash contact.
- Either transport the sample gas to a conditioning system or condition the sample at the port and transport the conditioned sample to the instrument.
- Condition the sample by reducing all forms of mercury in the sample gas to  $\text{Hg}^0$  and remove moisture from the sample gas.
- Measure the mercury in the flue gas sample.

Mercury analyzers can be distinguished by their measurement detection principle. Methods used include preconcentration by gold amalgamation with CVAAS detection, Zeeman-modulated CVAAS, preconcentration, and gold amalgamation with CVAAS detection. Instruments are also being developed based on AES and laser technologies.

### ***CVAAS Method***

The CVAAS method determines the mercury concentration in the gas by measuring the attenuation of the light produced by a mercury vapor lamp as it passes through a cell that contains the sample gas. The mercury atoms in the cell absorb mercury at their characteristic wavelength of 253.7 nm. Other flue gas constituents such as  $\text{SO}_2$  absorb light across a wide spectrum including the 243.7 wavelength, thus acting as an interferant. Water vapor and particulate are also broadband absorbers that must be dealt with in CVAAS measurement. One method to remove the interferants is to preconcentrate the mercury on a gold trap for a known period of time at a known flow rate. The gold trap is then heated, and the mercury is swept into the detection cell with an inert gas. A second method is to use a powerful magnet to slightly shift the wavelength of the mercury vapor lamp (Zeeman modulation). The broadband absorbers will attenuate the signal at both wavelengths, and the difference between the signals is attributed to the mercury concentration. A third method is to use two detection cells. The sample gas first passes through a cell, and the signal attenuation is measured. The sample gas then passes through a trap to remove the mercury and finally through a second cell to measure the attenuation caused by the interferants. Similar to the Zeeman-modulated method, the difference in signals is attributed to the mercury concentration.

### ***CVAFS Method***

Typically, the CVAFS method uses gold amalgamation to preconcentrate the mercury. After the mercury is desorbed from the trap, it is swept into the detection cell by an argon carrier gas. The mercury atoms in the cell are excited to fluorescence by a pulsed mercury discharge lamp, which is measured by a photomultiplier tube. The fluorescence results in increased selectivity since only the mercury atoms will fluoresce. The fluorescence can be quenched through collision of excited mercury atoms with other components of the sample gas, particularly oxygen and nitrogen. In cases where the mercury concentration is high, nitrogen may be used as the carrier gas to suppress the fluorescence signal.

### ***AES Method***

The AES method is currently being developed by EnviroMetrics for mercury measurement. The method is based on the emission of light from mercury atoms induced by a high energy source such as a plasma. The light is emitted at the characteristic 253.7-nm wavelength. The advantage of this method is that the electron energy can be optimized to produce more radiation from the mercury in the sample gas than any other constituent. The AES method also has the potential to be used as a multimetal monitor.

### ***Flue Gas Conditioning***

Both CVAFS- and CVAAS-type mercury analyzers can only measure elemental mercury. Therefore, to measure the total mercury concentration in a sample gas stream, the oxidized forms must be reduced to elemental mercury in a conversion system. The most common method of reducing oxidized forms of mercury to elemental is using a liquid reducing agent such as  $\text{SnCl}_2$  (stannous chloride). This method is used extensively, but has proven to be problematic. The wet-chemistry conversion systems are considered to be the limiting factor in reliability of Hg CEMs. The wet-chemistry systems use corrosive or caustic chemical solutions in large quantities. The spent reagents must be treated as hazardous waste which generates disposal concerns. In addition, all of the interactions between different flue gas constituents, the different mercury species, and the reducing reagents are not yet clearly understood.

Efforts to develop “dry” conversion units are beginning to produce results. These techniques center around using high-temperature catalysts or thermal reduction units to convert the oxidized mercury fraction to elemental mercury. These units also condition the sample gas by removing moisture and other interferants before the sample gas is sent to the analyzer. Although labeled as dry systems, most use chillers and gas–liquid separators to remove moisture from the sample gas stream. Demonstration of different dry units is ongoing, with early results looking favorable. There is some concern about the life and cost of catalysts used to reduce the oxidized forms of mercury to elemental mercury. Also, with the relative immaturity of this technology, it is likely that not all interferants and interactions with flue gas and the catalysts have been identified. Once proven, these units could greatly reduce the operational maintenance requirements.

## ***Particulate Removal***

Particulate-bound mercury captured on a filter can be reduced to  $\text{Hg}^0$ , but because of particulate matter transport issues, it is impractical. Also, EPA Draft Performance Specification 12A only requires CEMs to measure “the total concentration (regardless of speciation) of vapor phase mercury (11).” Therefore, it is important to remove any particulate matter from the sample gas stream in a manner that ensures it does not interfere with the operation of the analyzer or impart a bias to the mercury data. Conventional filtration methods will not work because as the particulate matter forms a dust cake on the filter media, it has a greater chance to interact with the flue gas and the mercury. The total mercury concentration could be biased low if the particulate matter is reactive and captures mercury. Although not important for measuring total mercury, the particulate matter on the filter could potentially bias the speciation of the measured mercury by oxidizing elemental mercury across the filter media. In an effort to greatly reduce or eliminate this problem, most CEM systems are either equipped with an inertial separation probe or a blowback filter of some type. In wet stack applications, downstream of a wet scrubber, water droplets in the stack make representative sample collection difficult. Mercury in the oxidized form could likely be associated with water droplets and not captured in isokinetic sampling. The EERC currently uses long heated probes upstream of a filter. The assumption is that mercury downstream of the scrubber would be elemental and, therefore, not significant in the water condensing in the stack.

## ***Calibration***

Regardless of measurement technique or conversion system, all instruments must be calibrated. All of the instruments available are easily zeroed by passing a filtered mercury-free sample gas through the analyzer. There are basically four ways to span a Hg CEM. First is manual injection of a known quantity of mercury. Since the vapor pressure of mercury is a well-known function of temperature, only the volume injected and the temperature of the vapor need be known in order to determine the amount injected. This is considered a primary standard for calibration. Second would be the use of a calibrated permeation source which may be internal or external to the instrument. These permeation devices can also be used to spike a sample at the inlet to the sampling probe to demonstrate the integrity of the sampling system. Third is the use of a calibration gas from a certified cylinder. The problem with cylinders is the high cost and low volume of gas in each cylinder. The last option (mainly for a CVAAS instrument using Zeeman modulation) involves using a small sealed cell with a known volume that contains a bead of elemental mercury. Again, the concentration in the cell is a function of the temperature of the cell. The cell is placed in the light path of the instrument, and the concentration is known based on the temperature of the cell.

## ***Commercially Available CEMs***

Table 1 provides a list of the commercially available Hg CEMs. A short description of each instrument is also provided. These descriptions are not meant to provide a detailed description, but simply an overview. The Web site for each vendor is provided.

## **Durag HM-1400 TR**

Web site: <http://www.durag.net/em/mercury/hm1400.html>

The Durag HM-1400 TR is a dual-beam nonconcentrating CVAAS instrument that uses a thermocatalytic converter to reduce oxidized mercury to elemental mercury. A heated sample probe (SP-2000) and heated sample line are used to transport the sample gas to a chiller where the moisture is removed. The ionic forms of mercury are then reduced in the thermocatalytic converter. The catalyst in the converter will also remove some of the SO<sub>2</sub> from the sample gas stream. The mercury in the sample gas is measured in one cell of the instrument then passes through a mercury scrubber before passing through a second cell which is used to determine the compensation for the SO<sub>2</sub> and NO<sub>2</sub> interferences. The required sample flow rate is 100–120 N L/hr. The measurement cycle time is listed as less than 3 minutes, with a measurement range of 0–45 µg/Nm<sup>3</sup> and a lower detection limit of <1 µg/Nm<sup>3</sup>. The measurement range can be expanded by diluting the sample gas stream. The sensitivity is listed as 0.2 µg/Nm<sup>3</sup>, with a total accuracy of ±1% full scale or ±5%, depending on which specification sheet you look at. Zero drift is less than ±1.4% full scale, and the span drift is less than 2% full scale after 6 months. Durag claims a 6–8-month maintenance cycle for the unit. Flue gas sampling was previously listed as an appropriate application for this instrument. However, the Durag Web site no longer lists flue gas sampling as an appropriate application.

## **EcoChem Analytics Hg-MK II**

Web site: <http://www.ecochem.biz/Mercury/AnalyzersHGMKII.htm>

The EcoChem HG-MK II uses CVAAS to detect elemental mercury in the gaseous phase. In order to measure total mercury, which includes mercuric chloride, the HG-MK II uses a patented dry thermocatalytic reactor to reduce oxidized forms of mercury to elemental mercury. No wet chemical reactors are used, and this greatly decreases complexity and maintenance requirements. After reduction, the sample stream is passed through a gold trap amalgamation unit where elemental mercury is absorbed. Subsequently, the mercury is desorbed from the gold trap into a stream of pure nitrogen and measured in a ultraviolet (UV) atomic absorption photometer operating at 253.7 nm.

**Table 1. Commercially Available Hg CEMs**

| Vendor                | Product       | Analysis Method     | Pretreatment/<br>Conversion         | Speciation              |
|-----------------------|---------------|---------------------|-------------------------------------|-------------------------|
| Durag                 | HM-1400 TR    | Atomic absorption   | Thermal catalytic                   | Hg <sup>total</sup> (g) |
| EcoChem Analytics     | Hg-MK II      | Atomic absorption   | Thermal catalytic                   | Hg <sup>total</sup> (g) |
| Envimetrics           | Argus-Hg 1000 | Atomic emission     | Thermal catalytic                   | Hg <sup>total</sup> (g) |
| Nippon                | DM-6          | Atomic absorption   | Thermal catalytic                   | No                      |
| Nippon                | DM-6A/MS-1A   | Atomic absorption   | Wet chemistry and thermal catalytic | Yes                     |
| Nippon                | DM-6B         | Atomic absorption   | Thermal catalytic                   | Yes                     |
| Nippon                | AM-2 or AM-3  | Atomic absorption   | Wet chemistry                       | Hg <sup>total</sup> (g) |
| Ohio Lumex            | RA-915+       | Atomic absorption   | None available                      | No                      |
| Opsis AB              | HG200         | Atomic absorption   | Dilution system                     | Yes                     |
| PS Analytical         | Sir Galahad   | Atomic fluorescence | Wet/dry chemistry (2004 or 2005)    | Yes                     |
| Semtech Metallurgy AB | Hg 2010       | Atomic absorption   | wet chemistry                       | Hg <sup>total</sup> (g) |
| Sick UPA GmbH         | MERCEM        | Atomic absorption   | Wet chemistry                       | Hg <sup>total</sup> (g) |
| ST2 Technologies      | SM-3          | Atomic absorption   | Thermal catalytic                   | Yes                     |
| Tekran, Inc.          | 3300          | Atomic fluorescence | Dilution system                     | Yes                     |

EcoChem claims that there are no interferences or cross sensitivities caused by exposure to flue gas. “The EcoChem HG-MK II uses a Gold Trap Amalgamation unit to capture the mercury present in flue gas, then transfer that mercury into a stream of pure nitrogen. Then when presented to the UV photometer, the measurement can be performed very accurately with interferences completely eliminated.” “By varying the collection time associated with the gold trap, it is possible to change the measuring ranges of the instrument. Thus for a hazardous or municipal waste incinerator, the EcoChem HG-MK II can operate in the range of 0 to 50 µg/m<sup>3</sup>. While for a coal-fired utility application, the collection time can be increased, and the measuring range may be 0 to 10 µg/m<sup>3</sup> or even 0 to 1 µg/m<sup>3</sup>.” The advertised resolution is 0.1 µg/m<sup>3</sup>.

All fittings and tubing in the instrument are made of Teflon, quartz, or glass. Areas where metal must be used incorporate “heated special alloys.” All surfaces coming in contact with oxidized mercury are held at elevated temperatures.

The system is controlled by a microprocessor, with all inputs made through a water-resistant front panel keyboard with user-programmable keys (“soft keys”). A large thin-film transistor (TFT) color screen displays all system variables and measured values. The most important components are housed in two 19-in. rack-mounted units each three units high. Other components can be accessed from the back plate of the housing.

The EcoChem HG-MK II executes an automatic zero-point and a reference-point procedure at preset intervals. Important process variables like flow rate, temperature, and instrument drift are continuously monitored. In case of excessive deviations from set values, a status signal is activated to alarm the operator.

The basic components of the HG-MK II include a probe with a heated line to transport the sample to the analyzer. The sample probe extracts 2 to 3 liters a minute and transports it through a heated sampling line at 200°C. In order to prevent loss of mercury in the sampling line, it is recommended that the line not exceed 150 feet. A thermocatalytic converter reduces oxidized mercury compounds to elemental mercury vapor. The amalgamation unit consists of an integrated valve assembly, a gold trap, and a calibration source for elemental mercury vapor. The valve assembly can be switched to “continuous mode operation” in case of high mercury concentrations. The gold trap amalgamation unit offers the ability to reduce the detection threshold by modifying the collection time. The UV photometer consists of a fixed-wavelength atomic absorption spectrometer at a 253.7-nm wavelength. The photometer has a reference beam for lamp control and an electrodeless low-pressure lamp with long service life (>20,000 hours).

EcoChem claims no interference from SO<sub>2</sub>, NO<sub>x</sub>, volatile organic compounds, and other compounds through the use of the gold trap. However, it does not mention if HCl causes interferences with the gold trap. Manufacturers of other instruments that use gold amalgamation acknowledge interference in the presence of HCl and NO<sub>x</sub>.

The instrument is zeroed automatically but also has manual correction for the zero point. The instrument is spanned either automatically or manually using permeation device.

### **Envimetrix Argus-Hg 1000**

Web site: [http://www.envimetrix.com/Env\\_Products.htm](http://www.envimetrix.com/Env_Products.htm)

The Argus-Hg 1000 uses atomic emission spectroscopy to measure total mercury in a flue gas stream. The particulate in the sample gas is removed by a ceramic blowback filter before it passes through a thermo catalytic converter which reduces all mercury in the sample gas to elemental mercury. A Peltier chiller is used to remove moisture from the gas before it is transported to the analyzer. In the analyzer, the sample gas first passes through an absorber which collects the mercury. When the absorber is heated, the mercury is swept into the detector with an argon carrier gas. The instrument will only consume one (200-ft<sup>3</sup>) tank of argon a year. Microwave energy is used to excite electrons in a plasma. The high-energy electrons then collide



with the mercury atoms in the sample gas causing them to radiate both visible and UV light. The electron energy has been optimized to produce a large amount of UV light from mercury and a minimal amount of UV light from all other species in flue gas, thus eliminating the effects of any interferants. Calibration of the analyzer is achieved with an internal permeation device, and there is no need for zero adjustment. The lower detection limit is advertised as  $0.03 \mu\text{g}/\text{m}^3$  with a 3-minute cycle time. Envimetrics participated in the second round of the EPA Environmental Technology Verification (ETV) Program (12).

### **Nippon DM-6**

Web site: <http://www.hg-nic.com/dmseries.html>

Nippon has four different analyzers for sampling flue gas from a coal-fired utility. The DM-6 is considered a “dry” system. In the pretreatment unit, DM-6P, the sample gas is drawn from the stack and passes through a filter to remove dust. The mercury compounds are then reduced to elemental mercury by contacting with the solid-state reduction catalyst which is housed in the probe. The sample gas with the reduced elemental mercury then passes through a chiller to remove the moisture (condensate is continuously pumped back into the stack) and then transported to the detector via Teflon tubing to be continuously measured by CVAAS. A liquid crystal display shows the mercury concentration which is updated every second. The detector unit has outputs for either an external computer and/or a data logger. The response time is less than 1 minute, and the sensitivity is listed as  $0.1 \mu\text{g}/\text{m}^3$ .

Horiba Instruments, Inc., of Irvine, California, has entered into a long-term agreement with Nippon Instruments Corp. (NIC) headquartered in Osaka, Japan, to exclusively sell and service the NIC Continuous Mercury Emissions Monitor in the United States. NIC has been designing and selling instruments to measure mercury in the environment for the last 25 years.

Nippon participated in the first two rounds of EPA ETV Program to evaluate Hg CEMs (12).

### **Nippon DM-6A/MS-1A**

Web site: <http://www.hg-nic.com/dmseries.html>

The DM-6A/MS-1A is similar to the DM-6, but it has the added capability of speciating the mercury in the sample gas stream. First, the sample gas is mixed with a solution that captures the oxidized forms of mercury. The sample then passes through a gas–liquid separator. A potassium hydroxide (KOH) scrubber is used to remove interference gases such as  $\text{SO}_2$ . The gas portion of the sample then passes through a chiller to remove moisture and then through the detector to give a measurement of gaseous elemental mercury in the flue gas stream. The solution containing the  $\text{Hg}^{2+}$  is mixed with a reducing solution ( $\text{SnCl}_2$ ) to reduced the oxidized mercury to gaseous elemental mercury. This sample stream then passes through a gas–liquid separator. This sample gas stream then passes through a KOH scrubber to remove interference gases. After dehumidification, the sample passes through the detector to give a measurement of oxidized mercury in the flue gas stream. The DM-6 and DM-6A both have a nominal range of

0.1–1000  $\mu\text{g}/\text{m}^3$ . Both are calibrated with an internal permeation device and have an automatic zero adjust.

### **Nippon DM-6B**

The DM-6B is essentially two DM-6 units running in parallel. The first unit operates as a DM-6 to give a measurement of total gaseous mercury. The second unit passes the flue gas through a chiller before passing through the catalyst. By doing this, the oxidized mercury is removed with the condensate, and the result is a measurement of the gaseous elemental mercury in the sample gas stream. This instrument is currently being evaluated by the EERC.

### **Nippon AM-2 or AM-3**

Web site: <http://www.smglink.com/nic/>

The AM-2/3 instrument uses gold amalgamation concentration techniques with CVAAS detection to measure mercury in a gas stream. In some areas, the AM-2/3 is still listed as appropriate for sampling mercury in a flue gas stream, but it appears it has been replaced by the DM-6 series instruments. The AM-2 was also evaluated during the first round of the EPA ETV Program (12).

### **Ohio Lumex RA-915+**

Web site: <http://www.ohiolumex.com/>

The Ohio Lumex RA-915+ is a real-time continuous monitor for total and elemental mercury measurement. The instrument is based on differential Zeeman atomic absorption spectroscopy using high-frequency modulation of light polarization. A mercury lamp is placed in a permanent magnetic field which has the ability to slightly change the wavelength of the mercury light. This allows for background correction for such broadband absorbers as  $\text{SO}_2$ , moisture, and particulate matter. The Lumex has a multipass cell which provides an effective path length of 10 meters. The instrument does not use gold amalgamation preconcentration which allows for a faster response time. In ambient air, a lower detection limit of 2  $\text{ng}/\text{m}^3$  can be achieved according to the manufacturer. Ohio Lumex provides a cell for thermal reduction of oxidized mercury to elemental mercury. No catalyst is used in the thermal decomposition cell. Further testing needs to be completed with this system to ensure recombination of the oxidized mercury does not take place.

The Lumex needs an external mercury supply such as a permeation device or a gas cylinder for calibration. The instrument does come with a small cell of fixed volume that contains saturated mercury vapor which can be used to check the calibration.

An earlier version of the Ohio Lumex instrument was evaluated during the first round of the EPA ETV Program (12).

## **Opsis Hg-200**

Web site: <http://www.opsis.se/monitoring/cemproducts.asp?Id=6>

The Hg-200 uses a dilution extraction system to provide a flue gas sample to the analyzer. Four 1/4-inch Teflon lines are used to connect the stack probe to the analyzer. One line carries dilution air to the probe, another transports diluted sample from the probe to the instrument, the third sends calibration gas from the analyzer to the probe, and the fourth is a vacuum sensor line for verifying that the sampling system is working. The sample gas is filtered before critical orifices are used to mix and dilute the sample gas. The nominal dilution rate is 100:1 which prevents condensation during transport to the analyzer. A pump is used to supply 2 L/min of sample gas to the analyzer. A thermocatalytic converter is used to reduce all of the mercury to the elemental form. The catalyst can be run hot or cold to give measurements of total or elemental mercury, respectively. The cycle time is normally 5 minutes. The analyzer portion of this system uses CVAAS and a double-beam photometer. The mercury is preconcentrated on a gold trap. An internal permeation device is used for span calibration of the instrument along with an automatic-zero adjustment. The lower detection limit of the instrument is listed as 0.05 ng/m<sup>3</sup>, with a nominal measurement range of 0.5–1000 µg/m<sup>3</sup>. The Opsis Hg-200 was evaluated in the first round of the EPA ETV Program (12).

## **PS Analytical Sir Galahad 10.665**

Web site: <http://www.psanalytical.com/>

The Sir Galahad analyzer utilizes a completely integrated sampling, conditioning, and analysis system to determine the mercury concentration in a flue gas stream. The sample gas is extracted from the duct using a heated inertial separation probe. The sample is then transported to a wet chemical system where the sample stream is split into two streams. The first stream is mixed with a KCl solution to remove the oxidized mercury from the sample gas stream. The gas passes through a chilled gas–liquid separator to remove moisture. It is then sent to the Sir Galahad analyzer for determination of mercury concentration. The second gas stream is mixed with a reducing solution which reduces all of the mercury in the sample gas stream to elemental mercury. It also passes through a chilled gas–liquid separator to remove moisture before being sent to the analyzer. A switching box is used upstream of the analyzer to select between sampling total Hg or Hg<sup>0</sup> and sending either zero gas or a span gas to the probe tip. The span gas is generated by the CavKit which is similar to a permeation device. The Sir Galahad analyzer utilizes gold amalgamation and CVAFS to determine the mercury concentration in the sample gas stream. A source of compressed mercury-free argon and clean, dry air is required for operation of the analyzer. If the mercury concentrations are high, mercury-free nitrogen can be substituted for the argon. Calibration of the system is done using Hg<sup>0</sup> as the primary standard. It is contained in a closed vial held in a thermostatic bath. The temperature of the mercury is monitored, and the amount of mercury is calculated using vapor pressure calculations. Typically, the calibration of the unit has proven to be stable over a 24-hr period. The sample cycle time is typically 6 minutes, and the nominal measurement range is 0.001–2500 µg/m<sup>3</sup>. PS Analytical has participated in both rounds of the EPA ETV Program (12).

## **Semtech Metallurgy AB Hg 2010**

The Semtech analyzer uses CVAAS with background Zeeman correction to determine the mercury concentration in a sample gas stream. Semtech offers a wet-chemistry conversion system to reduce oxidized mercury to elemental mercury. However, the conversion system only works if there is no SO<sub>2</sub> present in the sample gas. The lower detection limit can be changed by increasing the path length. Several sample cells are available, with the longest providing a 500-mm path length. With the 500-mm cell, the lower detection limit is 0.3 µg/m<sup>3</sup> and the upper limit is 160 µg/m<sup>3</sup>. The instrument automatically zeros every hour by pulling room air through a carbon filter and then through the detection cell. The span can be checked with a sealed cell of known volume which contains saturated mercury vapor. The concentration in the cell is only a function of the temperature of the cell. There are no set flow rate requirements for the Semtech. The Semtech Hg 2010 has been certified by TÜV Rheinland for determining compliance with the German legal limit of 50 µg/Nm<sup>3</sup> for total mercury emissions from waste incinerators.

## **SICK UPA GmbH MERCEM**

Web site: [http://www.maihak.de/sickmaihak\\_de/en.html](http://www.maihak.de/sickmaihak_de/en.html)

The TÜV-certified SICK MERCEM instrument uses CVAAS to detect elemental mercury in the gaseous phase. The MERCEM employs a sample probe containing two sintered metal filters to extract a particulate-free flue gas sample. A heated (185°C) sample line is used to transport the sample gas to the conditioner and analysis units. A tin(II) chloride (SnCl<sub>2</sub>) solution is injected into the sample line and transported concurrently with the sample gas to a reactor for converting oxidized mercury to elemental mercury. The concentration of SnCl<sub>2</sub> reducing solution is kept constant by refilling from a reservoir with a peristaltic pump.

After passing through a peltier cooler to remove moisture, the dry sample gas enters a gold trap for amalgamation. In the amalgamation procedure, a precisely defined volume of the sample gas is passed through a gold trap, and the elemental mercury forms an amalgam with the gold. At the end of this collection phase, the gold trap is heated electrically and the mercury is released and transported through the cell of the photometer by an inert carrier gas stream. Following the purging cycle, the gold trap is cooled and is then ready for the next collection period. By varying the collection period, the measurement range or the detection limit can be varied over a wide range to meet individual requirements. The recommended range is 0–100 µg/m<sup>3</sup>, with a detection limit of <0.5 µg/m<sup>3</sup>, depending on sampling time. Therefore, mercury can be accurately measured for a wide range of sources from hazardous waste incinerators to coal-fired power plants.

The amalgamation procedure features an additional major advantage, i.e., that the Hg analyzer is never in direct contact with the stack gas. Thus interferences caused by other components in the stack gas are eliminated. However, compared to other CVAAS systems, the response time is longer by approximately 180 s.

Although a relatively large unit, the MERCEM comprises a system cabinet containing the sample gas transfer lines, analyzer unit with sample gas preparation assembly, and control unit. All components inside the cabinet can be easily accessed for maintenance purposes when the

front door is open. The reservoir for the reductant solution is located directly behind the front door, making it very easy to replace.

The MERCEM is designed for continuous operation and contains all control units and self-check functions required for automatic operation. The temperature and flow rate of the sampling system are constantly monitored. The unit has an automatic zeroing system but calibration using elemental mercury is accomplished using an external source.

### **ST2 Technologies SM-3**

Web site: <http://www.mercury-instruments.de>

U.S. Distributor: ST2 Service Technologies, Inc., <http://www.st2-service.com>

The TÜV-certified Mercury Instruments SM-3 uses CVAAS to detect elemental mercury in the gaseous phase. A probe with a heated line and filter is used to transport the sample to the analyzer. In order to measure total mercury, which includes mercuric chloride, the SM-3 uses a patented dry thermocatalytic reactor to reduce oxidized forms of mercury to elemental mercury. No wet chemical reactors are used, and this greatly decreases complexity and maintenance requirements. After all the mercury in the flue gas has been reduced, the gas is passed to a peltier cooler and the water is condensed out. The dry gas is then fed to the mercury detector where the mercury concentration is measured using a UV atomic absorption photometer operating at 253.7 nm.

To prevent recombination and any adsorptional loss of mercury, all surfaces coming into contact with the sample gas are heated to temperatures  $>180^{\circ}\text{C}$ . The SM-3 does not use any gold collector for mercury preconcentration, thus giving a very fast response and providing results continuously and in real time. Possible problems connected with “poisoning” of the gold surface are thus eliminated.

The instrument has three operating ranges, 0–45, 0–75, 0–500  $\mu\text{g}/\text{m}^3$ , and a stated detection limit of  $<1\%$  of measuring range. The response time is  $<60$  seconds, compared to up to 6 minutes for systems using a gold trap. The zero drift is  $<1\%$ , and the instrument comes with an auto-zero feature. The instrument must be externally calibrated using a permeation tube or other such device. However, Mercury Instruments does sell an external calibration system (MC 3000) that works directly with the SM-3.

The system is controlled by a microprocessor, with all inputs made through a water-resistant keyboard. A large TFT color screen displays all system variables and measured values. The unit is housed in a single, relatively small unit ( $550 \times 1000 \times 700$  mm).

## **Tekran®, Inc., 3300**

Web site: <http://tekran.com/phpcode/index.php>

The Tekran® Series 3300 speciating mercury continuous emissions monitor uses a CVAFS analyzer in conjunction with a dry conversion system and sampling probe to measure speciated mercury in a flue gas stream. The sample gas is pulled through a stack-mounted high-flow-rate inertial probe to minimize mercury measurement artifacts due to filtering. The sample is then diluted and transported through a heated line to a conditioning module. The diluted sample is split into two streams. In the first stream, a thermal conditioner unit reduces all of the mercury forms present in the sample to elemental mercury. Recombination is avoided by the quantitative removal of HCl and other gases by a patented thermal conditioner/scrubber system. The second pathway removes ionic (water-soluble) mercury, leaving only the elemental mercury to pass through to the converter. This stream is then subjected to additional conditioning to remove acid gases and excess humidity from the sample. Ionic mercury is determined by difference. This conversion unit has the advantage of not using chemical reagents or solid sorbents.

The probe is capable of performing automated filter blowback, multipoint calibrations, and standard additions of elemental mercury into the sample matrix. Probe temperatures, flow rates and pressures are monitored and telemetered to the system controller via a datacom link.

The two conditioned streams are analyzed using a Tekran Model 2537A mercury vapor analyzer. This analyzer is in wide use all over the world and has demonstrated its accuracy, stability, and reliability under the most remote and rugged conditions imaginable. The analyzer uses gold preconcentration combined with atomic fluorescence detection. The advertised minimum detection limit for the analyzer is less than  $0.05 \mu\text{g}/\text{m}^3$ . A source of compressed mercury-free argon is required for operation of the instrument.

A calibration source allows both multipoint calibrations and standard additions to be automatically initiated. Both these operations are performed through the entire CEM path, including all probe filters. The calibration unit generates concentrations of mercury by using a National Institute of Standards and Technology-traceable temperature-controlled saturated mercury vapor source. Precision mass flow controllers are used to dilute the output of this source to the desired value. The unit is capable of continuously generating large flow rates of calibration gas at no ongoing cost – unlike expensive mercury calibration gas cylinders.

The computer provides full control of each module within the system. Industry standard protocol is used to monitor and control each unit. All temperatures, flows, and pressures are displayed by the application program and may be set by authorized users. The system features remote operation and problem diagnosis, either via a modem and telephone line or through the Internet.

## SUMMARY

Hg CEMs are necessary and useful tools for measuring mercury for both research and compliance applications, and a variety of instruments are available, each with unique advantages and drawbacks. Measurement of mercury in a flue gas stream generated by coal combustion is much more challenging than measuring from other sources. Sources such as incinerators typically have more pollution control equipment such as scrubbers in conjunction with fabric filters and sorbent beds which all help to clean up the flue gas before it reaches a mercury measurement system. However, development is ongoing to address the challenges to providing long-term operation for flue gas monitoring with a minimal amount of maintenance. All of the analyzers mentioned will measure mercury in a relatively clean sample gas stream. The main challenge facing mercury CEM manufacturers is providing a “clean” sample gas to the mercury analyzer. The sample conditioning methods currently available are:

- Wet chemistry – These systems provide speciated mercury data by using wet chemistry methods to either remove or reduce oxidized mercury from the sample gas as well as remove interferant gases from the sample gas stream. To date these have been the most frequently used systems for research and there has been a great deal of data collected while using them. The reliability of these systems has been improved through several design iterations, but they still require more maintenance than is acceptable for long term monitoring. Because these systems are wet chemistry based they require large amounts of chemicals and generate a large amount of waste (up to 8 liters per day). The wet chemistry systems have worked well in plants burning either lignite or subbituminous coal. However, in plants burning bituminous coal with high sulfur and chlorine, there have been problems with the chemistry of the system. Some plants with high SO<sub>2</sub> also generate high SO<sub>3</sub> concentrations. The SO<sub>3</sub> can pass through the wet chemistry portion of the system as an aerosol and deposit on backup filters and sample lines. This can cause problems with mercury capture and changes to speciation. The wet chemistry systems can be used with any type of mercury analyzer.
- Thermal Catalytic Reduction – These systems can provide speciated mercury data. The oxidized forms of mercury are reduced to elemental mercury across a catalyst bed. A dry sorbent or wet chemistry system may be used to remove oxidized mercury from the sample gas stream. These systems may include additional wet chemistry systems for removing interferants from the gas stream before sending the gas to the analyzer. The volume of wet chemicals consumed in these systems is much smaller than the all wet systems (on the order of a liter per week). Limited long-term data has been generated using these systems. However, there appears to be problems with the life of the catalysts particularly in high acid gas situations. The catalysts are expensive and may need frequent regeneration and or replacement. The thermal catalytic systems have yet to demonstrate long-term reliability. It is most likely that not all of the interferants and interactions with different flue gas components have been identified. Thermal catalytic reduction is best used with the CVAAS analyzers because the interferant gases for CVAFS are not necessarily removed.
- Dilution and Thermal Catalytic Reduction – This is a relatively new method for conditioning the sample gas for mercury analysis. These systems dilute the sample gas

at or near the probe before sending it to a sample conditioner. The theory is that the diluted sample is easier to transport, and condition. The lower concentrations of interferant gases are also less likely to poison the catalyst used for reducing oxidized mercury to elemental mercury. Speciating the mercury is accomplished by scrubbing the oxidized mercury from the sample gas with a small amount of de-ionized water or a dry trap. Again, it is most likely that not all of the interferants and interactions with different flue gas components have been identified. Because of dilution and the resulting low mercury concentrations, a CVAFS analyzer must be used. These systems are the latest iteration of conditioning systems and not much data have been generated with them, but they have the potential to be very reliable with low maintenance requirements.

At this time there does not appear to be one instrument or measurement technology that will work best in all applications. However, the latest iteration of systems becoming available this summer show promise. The most advanced systems are those that integrate all of the components necessary to accurately and reliably measure mercury emissions from a utility boiler. These components include:

- Particulate removal system-It must continuously remove particulate matter before it can interact with the sample gas.
- Sample transport-Integrated with sample probe
- Sample conditioning system-Must provide “clean” dry sample gas to the mercury analyzer.
- Mercury analyzer
- Calibration/spiking system-Easy, preferably automatic calibration checks. Spiking of at least elemental mercury at the probe. Dynamic spiking of elemental mercury into the flue gas matrix at the probe is a plus.

As instrument improvements occur, updated reviews of their performance in demonstration tests will be provided in future quarterly reports to provide the reader with the information necessary to identify instruments best suited for their application and needs.



## UPCOMING EVENTS

Emission Monitoring 2004 – A seminar providing independent and objective perspectives for meeting emission monitoring and testing challenges

June 2–4, 2004, Durham, North Carolina

<http://www.emissionmonitoring.com>

Principles, Applications, and Opportunities with Activated Carbons

Professional Analytical and Consulting Services – Dr. Nowicki will provide a 2-day short course for \$950

June 17–18, 2004, Toronto, Ontario, Canada

<http://members.aol.com/hnpacs/news/MercurySorbentOpp.htm>

International Conference on Mercury as a Global Pollutant

June 7–July 2, 2004, Ljubljana, Slovenia

[http://congress.cd-cc.si/icmgrp04/?menu\\_item=welcome&menu\\_level=2](http://congress.cd-cc.si/icmgrp04/?menu_item=welcome&menu_level=2)

Air & Waste Management Association 97th Annual Conference and Exhibition

June 22–25, 2004, Indianapolis, Indiana

<http://www.awma.org/ACE2004/>

228th ACS National Meeting – Fall 2004

August 22–26, 2004, Philadelphia, Pennsylvania

<http://oasys.acs.org/oasys.htm>

EPRI–EPA–DOE–A&WMA Power Plant Air Pollutant Control “Mega” Symposium August 30–September 2, 2004, Washington, D.C.

Sign-up deadline April 15, and final presentations due July 23, 2004

<http://www.awma.org/events/mega.pdf>

14th International Activated Carbon Conference

October 7–8, 2004, Pittsburgh, Pennsylvania

<http://members.aol.com/hnpacs/conferences/IACC11techSum.htm>

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## REFERENCES

1. A State-of-the-Art Review of Flue Gas Mercury Speciation Methods; TR-107080; EPRI: Palo Alto, CA, and United States Department of Energy: Pittsburgh, PA, 1999.
2. Myshkin, A.E.; Konyaeva, V.S. Complex Formation of Hg (II) with Tris (Hydroxymethyl)Aminomethane. *Russian Journal of General Chemistry* **1994**, 64, 1722–1726.
3. *Evaluation of Flue Gas Mercury Speciation Methods*; TR-108988; EPRI: Palo Alto, CA, and United States Department of Energy: Pittsburgh, PA, 1999.
4. *Power Plant Validation of the Mercury Speciation Sampling Method*; TR-112588; EPRI: Palo Alto, CA, and United States Department of Energy: Pittsburgh, PA, 1999.
5. U.S. Environmental Protection Agency. Method 301 - Field Validation of Pollutant Measurement Method from Various Waste Media. In *Code of Federal Regulations*, Title 40, Parts 61 to 80; Office of the Federal Register: Washington, DC, July 1993; Part 63, Appendix A, pp 324–331.
6. J., Lu; Schroeder, W.H.; Berg, T.; Munthe, J.; Schneeberger, D.; Schaedlich, F. A Device for sampling and determination of total particulate mercury in ambient air. *Anal. Chem.* **1998**, 70, 2403.
7. Laudal D.L; Thompson, J.S.; Dunham, G.E.; Pavlish, J.H.; Galbreath, K.E.; Weber, G.F.; Sondreal, E.A. *Mercury Studies, Appendix B*; Final Report for U.S. Environmental Protection Agency Cooperative Agreement No. R-828323-01, U.S. Department of Energy National Energy Technology Laboratory Cooperative Agreement No. DE-FC26-98FT40321, and Ontario Power Generation; Energy & Environmental Research Center: Grand Forks, ND, Nov 2002.
8. U.S. Environmental Protection Agency. Draft Method 324 – Determination of Vapor-Phase Flue Gas Mercury Emissions from Stationary Sources Using Dry Sorbent Trap Sampling; In *Code of Federal Regulations*, Title 40, Parts 63, Appendix A.
9. Parker, B. European Mercury Monitoring Trip Report U.S. Environmental Protection Agency Office of Air Quality Planning and Standards Emission Measurement Center: Research Triangle Park, NC, Oct 10, 2000.
10. S.J., Hedges; Ryan; Stevens. Workshop on Source Emission and Ambient Air Monitoring of Mercury. September 13–14, 1999, Bloomington, MN, U.S. Environmental Protection Agency National Risk Management Research Laboratory, Cincinnati, OH, June 2000, EPA/625/R-00/002.
11. U.S. Environmental Protection Agency. Draft Performance Specification-12A Specification and Test Methods for Total Vapor Phase Mercury Continuous Emission

Monitoring Systems in Stationary Sources, In *Code of Federal Regulations*, Title 40, Part 60, Appendix B.

12. <http://www.epa.gov/etv/verifications/vcenter1-11.html>